Karl-Winnacker-Institut High Temperature Materials

Oxidation resistance improvement of low Al-content TiAl alloys by the halogen effect

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Funded by: AiF
Period: 01.04.2005 - 31.07.2007

Introduction

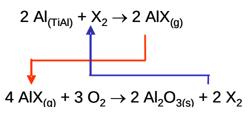
The alloys on the basis of TiAl open up new possibilities in the high-temperature technology (turbine blades for aeronautics, engine valves for automobiles...) due to their mechanical characteristics at high temperatures. However their use at temperatures above 700 °C is limited by their oxidation resistance. In order to improve their oxidation resistance, fluorination of the alloy was accomplished by halogen ion implantation into the metal subsurface. The halogen effect improves the oxidation resistance by promoting of growth an Al_2O_3 protective layer growth. Up to now the halogen effect was mainly applied to alloys with compositions close to 50 At.% aluminium. The goal of this project was to examine the potential of the halogen effect for alloys with Al-contents less than 48 At. %.

Thermodynamic calculations [1]

➢ Halogen effect: selective reaction of Al with the halogen (Fig 4a)

The main conclusions of the thermodynamic calculations using the software ChemSage are:

✓ same effect for Al contents between 40 and 50 at.%,
✓ “F-window” increases with temperature (Fig 4b)
✓ “F-window” decreases with decrease of the Al-activity
✓ the results for F and Cl are similar



$2\ Al_{(TiAl)} + X_2 \rightarrow 2\ AlX_{(g)}$

$4\ AlX_{(g)} + 3\ O_2 \rightarrow 2\ Al_2O_{3(s)} + 2\ X_2$

Fig 4a. Simplified mechanism of the halogen effect s

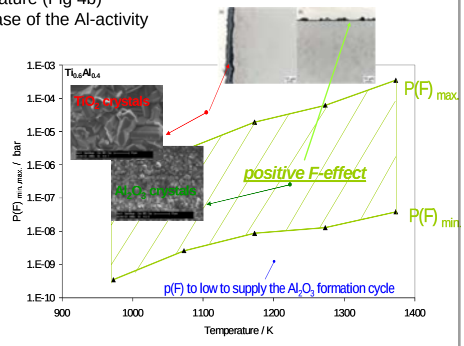


Fig 4b. Evolution of the fluorine partial pressure range (“F-window”) vs. temperature where a positive effect is expected (alloy $Ti_{0.6}\ Al_{0.4}$)

Implantation parameters

Halogen ions are extracted from a cold cathode ion source out of the gas phase. For generating $^{19}F^+$ ions, CF_4 is used as source gas. The ions are accelerated and focused to form a beam. Focusing is adjusted to maximum current on the substrate. To ensure homogenous implantation, the beam is scanned in front of the last aperture. The quantity of ions, the fluence, is measured directly via the current on the substrate. In ***Fig.1*** a T-DYN simulation is plotted to show the proportional relation between the ion fluence and the implanted dose. By penetrating the surface, ions loose their energy till they are stopped. In a first approximation, the resulting depth profile is a Gaussian-distribution around the mean penetration depth. There are multiple mechanisms of stopping ions in matter; for $^{19}F^+$ and in our energy range (20 keV up to 60 keV) *nuclear stopping* (elastic impact with target nuclei) and *electronic stopping* (ion looses its electrons due to inelastic impact with target electrons) are of the same order of magnitude. Nuclear stopping is theoretically found to be decreasing with ion energy, while electronic stopping is increasing with it. Both increase with ion atomic number. The implication of an increasing ion energy in the case of $^{19}F^+$ is shown in ***Fig.2***. So far only simulations for stoichiometric TiAl are shown. ***Fig.3*** sketches a comparison of stoichiometric TiAl and two other alloys containing niobium. By increasing the target density, the depth profile is shifted to lower penetration depths. However, the increase from 3.6 g/cm³ to 5.2 g/cm³ target density has only a slight effect on the mean penetration depth. The graphs above show Monte-Carlo ***simulations of ion implantation*** calculated with the software T-DYN.

Fig.1: influence of **ion fluence**

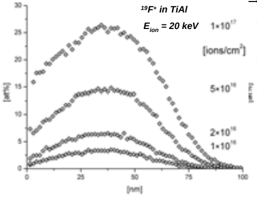


Fig.2: influence of **ion energy**

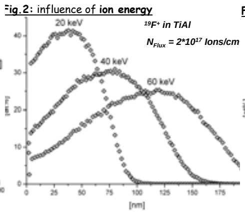
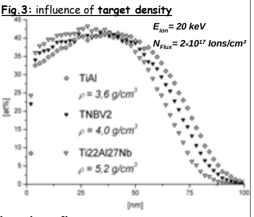


Fig.3: influence of **target density**



- ➢ implanted ion dose is proportional to ion fluence
- ➢ increasing ion energy will increase penetration depth
- ➢ increasing ion atomic number will decrease penetration depth
- ➢ only slight change in depth profiles for heavier TiAl-alloys containing Nb

Exposure tests with F-implanted technical alloys

Exposure tests were carried out in laboratory air over 4000 h with implanted samples under isothermal conditions at 900 °C.

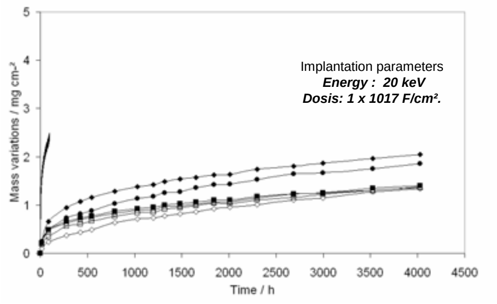


Fig 5. Mass change of implanted specimens for isothermal oxidation at 900 °C for 4000h under laboratory air. (black line) untreated γ-MET 100, and F-treated samples (◇) γ-MET 100 (◆) TNBV2A, (●) TNBV3, (■) TNBV3B,(△) TNBV3A, (□) TNBV2B.

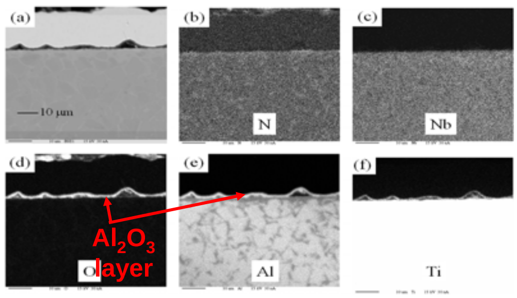


Fig 6. Typical composition mapping of the cross-section of the F-implanted side (sample TNBV2A) after an oxidation test at 900 °C for 120 hours in lab air.

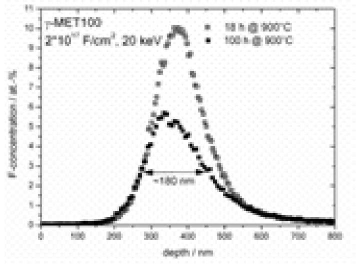


Fig 7. F-profile measured by PIGE after 18 and 100 h of oxidation at 900 °C in lab air.

For successful fluorine treatment it was shown that F stays localized at the oxide/metal interface even after oxidation [5]. Assuming a parabolic mass change with time the kinetic constants were derived from discontinuous TGA measurements (Table 1). Values obtained are typical of an alumina layer growth at 900 °C.

10^{13} x kp	TNBV2A	TNB2B	TNBV3	TNBV3A	TNBV3B	γ-MET	Al_2O_3
g² cm⁻⁴ s⁻¹	2.66	1.25	2.49	1.21	1.28	1.23	0.1-5 [4]

Table 1: Kinetic constants of different alloys at 900 °C (this work) [3]).

Conclusions

✓ the halogen effect is sustained over 4000 h under isothermal conditions at 900 °C
✓ growth of a stable and adherent almost pure alumina layer occurs
✓ positive effect for Al contents higher than 40 at.% with fluorine and chlorine
✓ better oxide scale adhesion with fluorine under laboratory air

References

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Conclusions

The halogen effect was obtained with fluorine for implanted technical alloys whose aluminium content was higher than 40 at. % for up to 4000 hours of oxidation in laboratory air. For fluorine profile simulations, it has been shown that the presence of alloying elements, e.g. Nb, does not drastically modify the fluorine profiles and implantation paramters may be kept constant. On the basis of cross-sectional observations, after 120 h at 900 °C in laboratory air, a pure 3-4 µm Al_2O_3 layer is found on the F-implanted side of the sample whereas a 10-15 µm Al_2O_3 + TiO_2 mixed oxide layer is present on the non-implanted side. It was shown that the halogen effect was effective over 4000 h (~ 1/2 year) at 900 °C under isothermal conditions leading to the formation of a dense, adherent and protective alumina layer.